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⑤ Microencapsulated flavoring agents and methods for preparing same.

⑦ The present invention pertains to a microencapsulated flavoring agent in the form of a spheroidal microcapsule which comprises a core and a coating layer over the core, wherein the microcapsule comprises (A) a core present in an amount up to about 90%, by weight of the microcapsule, which comprises (a) a flavoring agent in an amount from about 20% to about 80%, by weight of the core, and (b) a resin in an amount from about 80% to about 20%, by weight of the core, and (B) a coating layer over the core which comprises in percentages by weight of the coating layer, (a) gelatin in an amount from about 45% to about 49%, (b) gum arabic in an amount from about 45% to about 49%, and (c) glutaraldehyde in an amount from about 2% to about 10%. The encapsulated flavoring agents may be used in a wide variety of ingestible compositions and chewing gum products. The present invention also pertains to methods for preparing the encapsulated flavoring agents and the ingestible compositions in which they may be employed.

This invention pertains to microencapsulated flavoring agents prepared by complex coacervation. More particularly, this invention pertains to microcapsules containing a core comprising an emulsion of a flavoring agent and a resin and a coating layer over the core comprising a mixture of hydrocolloid materials. The microencapsulated flavoring agents may be utilized in a wide variety of edible compositions.

5 Microencapsulated flavoring agents are agents in the form of microcapsules which contain a core of flavoring agent and a coating layer over the core to control the release of the flavoring agent in a predetermined and predictable manner. In addition to providing sustained release flavor and uniform flavor intensity, microencapsulation of flavoring agents also provides protection for the flavoring agent from moisture, light, oxidizing agents, and other environmental factors.

10 Microencapsulation also permits the physical and chemical characteristics of a flavoring agent such as a flavor oil to be changed. For example, the hydrophobic properties of flavor oils cause the oils to irreversibly bind to gum base and certain confectionery bulking agents resulting in loss of flavor intensity and nonuniform mixtures. Conversion of such flavor oils to flavor powders by encapsulation can prevent such binding.

15 United States patent no. 4,597,959, issued to Barr, discloses a method for releasing flavor material in a breath freshener which comprises forming a wafer of microencapsulated droplets in an adhesive carrier. The microencapsulated droplets comprise liquid flavoring material in an amount from 85% to 90% and an encapsulating material of cross-linked gelatin and gum arabic in an amount of 5% to 15%, by weight.

20 United States patent no. 4,568,560, issued to Schoebel and assigned to Warner-Lambert Company, discloses a method for preparing a controlled release encapsulated active agent which comprises spray coating the active agent with a coating composition comprising a water-insoluble film-forming agent, an enteric agent, and a plasticizing agent.

25 United States patents no. 3,949,096, issued to Johnson et al. and assigned to SCM Corporation, discloses an improvement in a process for spray drying encapsulated particles which comprises cooling the spray dried particles while suspended in a stream of gas to prevent agglomeration. The coating materials in the process may be a saccharide material, proteinaceous material, edible gums and starches, edible waxes, edible resins, and normally solid lipoidal material.

30 United States patents no. 2,809,895 and no. 3,041,180, both issued to Swisher and assigned to Sunkist Growers, Inc., disclose a process for preparing an essential oil solid emulsion which comprises heating and melting a corn syrup solids solution, then adding to the melt a dispersing agent, and an essential oil containing an oil antioxidant, and then emulsifying and drying the resulting composition.

United States patent no. 4,610,890, issued to Miller et al. and assigned to Sunkist Growers, Inc., discloses a process for preparing an extruded essential oil solid emulsion which comprises heating an aqueous mixture of a sugar, a starch hydrolysate and an emulsifier, then admixing an essential oil to the aqueous mixture, and extruding the homogeneous melt into a cool solvent.

35 United States patent no. 3,949,096, issued to Barnes et al. and assigned to SCM Corporation, discloses a particulate composition comprising a matrix composition with up to about 40% loading wherein the matrix comprises from about 5 parts to about 95 parts maltodextrin and from about 95 parts to about 5 parts of hydrogen octenyl butanedioate amylopectin.

40 United States patent no. 3,949,096, issued to Johnson et al. and assigned to SCM Corporation, discloses a composition comprising a coconut core coated with a mixture of sugar particles and sugar particles encapsulated in edible fat.

45 United States patent no. 3,949,096, issued to Koene et al. and assigned to Naarden International N.V., discloses a process for flavoring dry vegetable matter which comprises mixing the vegetable material with a microencapsulated flavoring agent and an adhesive solution. The microencapsulated flavoring agent consists of droplets of flavor oils coated by an envelope of edible hydrocolloids.

United States patent no. 3,704,137, issued to Beck, discloses a process for preparing a particulate flavor oil which comprises mixing and heating an aqueous mixture of sucrose, hydrolyzed cereal solids and an emulsifier, then admixing an essential oil, and extruding and cooling the melt.

50 United Kingdom patent application no. 2,204,553A, to National Research Development Corporation, discloses microcapsules prepared by coacervation wherein the coating material comprises gelatin and polysaccharide XM6 obtained from bacteria.

55 Thus, a variety of encapsulated flavoring agents are known which have specific flavoring intensities and properties. There is still a need, however, for flavoring compositions which have varying properties, enhanced flavoring intensities and delayed sustained release properties for use in ingestible compositions. Such encapsulated flavoring agents would control flavor release and would permit an ingestible composition to contain a reduced total amount of flavoring composition and thereby reduce costs, and stability problems. The present invention provides such encapsulated flavoring agents and the ingestible compositions and chewing gum products in which the encapsulated flavoring agents may be used.



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<b>(21) International Application Number:</b> PCT/IB98/01551  <b>(22) International Filing Date:</b> 5 October 1998 (05.10.98)  <b>(30) Priority Data:</b> 08/947,694                      8 October 1997 (08.10.97)                      US  <b>(71) Applicant:</b> GIVAUDAN ROURE (INTERNATIONAL) S.A. [CH/CH]; 5, chemin de la Parfumerie, CH-1214 Vernier (CH).  <b>(71)(72) Applicant and Inventor</b> ( <i>for AT BE CH CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE only</i> ): SOPER, Jon, C. [US/US]; 1037 Mulford Road, Lebanon, OH 45036 (US).  <b>(72) Inventors:</b> KIM, Young, D.; 8855 Steeplechase Way, West Chester, OH 45069 (US). THOMAS, Margaret, T.; 832 Revere Village Court, Centerville, OH 45069 (US).  <b>(74) Agents:</b> JOSEPHIC, David, J., et al.; Wood, Herron & Evans, L.L.P., 2700 Carew Tower, Cincinnati, OH 45202 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> METHOD OF ENCAPSULATED FLAVORS AND FRAGRANCES BY CONTROLLED WATER TRANSPORT INTO MICROCAPSULES  <b>(57) Abstract</b>  A method of encapsulating an amphiphilic flavor or fragrance compound into a microcapsule having a hydrogel shell and an oil core. The flavor or fragrance compound is transported into and solubilized in the core by partition coefficient equilibrium using water in the capsule wall to transport the compound into the core. Microcapsules made by the method of the invention may have a wall thickness and contain a high concentration of the flavor or fragrance compound that has not previously been feasible.		

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## **METHOD OF ENCAPSULATING FLAVORS AND FRAGRANCES BY CONTROLLED WATER TRANSPORT INTO MICROCAPSULES**

### **FIELD OF THE INVENTION**

This invention relates to a method of encapsulating flavors or fragrances into microcapsules having a hydrogel shell and an oil core.

### **BACKGROUND OF THE INVENTION**

5                   Microcapsules incorporating a flavor or fragrance compound are useful to provide a controlled release of the contained flavor or fragrance. Such products may be used in the food processing industry, where encapsulated flavor particles may provide a flavor burst upon chewing the food. Such products may also be used in the  
10   cosmetic and toiletry industries, where encapsulated fragrance particles may provide a burst of scent upon capsule fracture. The capsule may comprise a shell surrounding a core material in which the flavor or fragrance compound is contained.

                  Microcapsules may be formed by a coacervation or  
15   crosslinking process, in which lipids are coated by tiny droplets of proteins, carbohydrates, or synthetic polymers suspended in water.

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The process of coacervation is, however, difficult to control and depends on variables such as temperature, pH, agitation of the materials, and the inherent variability introduced by a natural protein or carbohydrate.

5                   In the manufacture of microcapsules containing a flavor or fragrance compound, several features are desirable. It is desirable to produce microcapsules that have strong walls and that do not agglomerate. It is desirable that the compound be readily loaded into an oil microparticle, that is, be readily absorbed into the oil core of the  
10 microcapsule. Once absorbed, it is also desirable that the compound be irreversibly retained in the oil core of the microcapsule, that is, be adsorbed into the microcapsule.

                  The amount of compound that may be encapsulated depends upon several factors including its solubility in water, partition  
15 coefficient, molecular weight, water content, volatility, and the ratio of blank capsule to water amounts. Flavors and fragrances may be mixtures of hundreds of components, each of which may widely in these properties. A flavor or fragrance compound that is lipophilic may be readily contained in an oil core of a microcapsule, while a flavor or  
20 fragrance compound that is hydrophilic may be less readily contained in an oil core. For example, the flavor compound diacetyl (DA) is about 20% to about 30% water soluble. For diacetyl, typical maximum absorption into an oil is up to only about 55%. A highly water soluble

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compound such as diacetyl is also more difficult to retain in the oil core once it is loaded.

A compound's solubility in an aqueous phase versus an oil phase is determined by its partition coefficient, abbreviated as K. The partition coefficient of a compound is the ratio of the compound's concentration in one liquid phase to the compound's concentration in another liquid phase. The partition coefficient thus is an inherent property of the compound with two given liquid phases, such as a lipid phase and an aqueous phase, and reflects the compound's distribution at equilibrium between the water phase and the lipid phase. Any means of decreasing the water solubility of a compound will shift the equilibrium of the compound and thus shift its partitioning between an aqueous phase and a lipid phase. For example, addition of a salt will decrease the water solubility of a compound and will increase its partitioning into the lipid phase. Similarly, crosslinking a protein membrane to strengthen the membrane and physically decrease the amount of water, or physically removing water from the environment, causing capsule wall or membrane shrinking, will decrease the water solubility of a compound and will increase its partitioning into the oil phase.

Flavors or fragrances that are water soluble may interfere with encapsulation of an oil particle. For example, flavor or fragrance compounds that are water soluble cannot be encapsulated using gelatin

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coacervation. This is because for coacervation to occur, there must be a droplet to coat, and for these water soluble materials, there are no droplets to coat. In addition, the water soluble flavor or fragrance may partition so as to locate the flavor or fragrance compound in an

5 aqueous environment outside the encapsulated oil particle rather than inside the oil particle. If a flavor or fragrance compound is too water soluble, the coacervation process ceases to function due to the colloid becoming either too thick or too thin. A colloid that is too thick has no flow, and thus cannot properly coat the oil surface. A colloid that is

10 too thin is not retained on the oil surface. In the extreme, a water soluble flavor or fragrance compound can totally solubilize the colloid, leaving no wall material to deposit on the oil surface.

Besides water solubility, a flavor or fragrance compound that contains fatty acids affects the pH of a coacervation reaction. If a

15 base is added in an attempt to adjust pH, the fatty salts produced in the reaction impart an undesirable soap taste to a flavor compound. If a flavor or fragrance compound contains water soluble esters, the coacervation temperature is affected and hence the final gelation temperature is altered. While it is therefore desirable to limit

20 compounds that contain either fatty acids or water soluble esters, there is a tradeoff in the potency and profile results for the encapsulated compound. This limits the range of formulations that are able to be effectively encapsulated.



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Currently, flavor or fragrance compounds that are difficult to encapsulate are diluted with oils such as vegetable oil or mineral oil. This alters its oil to water partition coefficient, in which the compound attempts to reach an equilibrium between the oil and aqueous phases.

5 The oil serves to reduce the natural water solubility of most compounds and, in many cases, reduces it below the level at which it interferes with coacervation. A flavor or fragrance compound that is highly water soluble, however, does not have this effect. A compound that has a water solubility greater than 25% prefers to partition in an aqueous  
10 phase, and a ratio of lipid:water greater than 90% is needed to encapsulate these compounds. The coacervation process, however, is generally limited to about 22% lipid. Thus, this technique is of only limited applicability for water soluble flavor or fragrance compounds.

Several techniques are known in the art for absorbing  
15 compounds into a microcapsule, such as cyclodextrin entrapment or silica plating. A drawback of the cyclodextrin entrapment technique is that the binding effect varies widely depending upon the particular flavor or fragrance compound. A drawback of the silica plating technique is that there is no barrier to protect the flavor or fragrance  
20 compound from evaporation. Thus, there is a need for an efficient method of absorbing the many types of flavor and fragrance compounds to the desired level of loading in an encapsulated oil. There

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is also a need for an efficient method of adsorbing flavor and fragrance compounds once they have been encapsulated.

### SUMMARY OF THE INVENTION

This invention relates to a method of encapsulating a  
5 flavor or fragrance compound by controlled water transport of the  
compound into a capsule having an oil core. The method comprises  
preparing a microcapsule having a hydrogel shell and an oil core, and  
thereafter adding an amphiphilic flavor or fragrance compound in the  
presence of water to the microcapsule to transport the compound  
10 through the hydrogel shell and into the oil core. The compound is  
transported into the core by aqueous diffusion through the hydrogel  
shell. The oil core is retained in the hydrogel shell during the aqueous  
diffusion. A flavor or fragrance compound is thus encapsulated in the  
hydrogel shell containing the retained oil core.

15 The shell may consist of a carbohydrate or a protein,  
which may be crosslinked or non-crosslinked, or a synthetic polymer  
such as polyvinyl pyrrolidone or methyl cellulose. The oil core may  
comprise, for example, vegetable oil, mineral oil, benzyl alcohol, or  
mixtures thereof. In a preferred embodiment, the oil is a short chain  
20 triglyceride of fractionated coconut oil. As more particularly defined  
hereinafter, "oil" is meant to include a wide range of substances that  
are dispersible in water due to their hydrophobic nature.

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In an alternative embodiment of the invention, the microcapsule may be prepared in a dry form. An amphiphilic flavor or fragrance compound is added, in the presence of a controlled volume of water, to a substantially dry microcapsule having a hydrogel shell surrounding an oil core. The compound is transported through the hydrogel shell by aqueous diffusion into the oil core and is retained in the core. The microcapsule having the flavor or fragrance compound retained in the oil core is then dried.

In a preferred form of the invention, a flavor or fragrance compound is encapsulated by preparing a microcapsule of a coacervate of an oil core and a hydrogel shell, adding the flavor or fragrance compound in the presence of water to the microcapsule for transportation of the compound into the oil core, transporting the compound through the hydrogel shell by aqueous diffusion, and retaining the oil core in the hydrogel shell during the transportation to provide the encapsulated flavor or fragrance and retained oil core in the hydrogel shell.

The invention is also directed to the products produced by the methods of the invention.

One advantage of the invention is that the microcapsule may contain a concentration of the flavor or fragrance compound that heretofore has not been feasible. A second advantage is that the walls of the blank microcapsules have a substantially uniform thickness,

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strength, and resiliency. Another advantage is the increased yield of encapsulated flavor or fragrance, since essentially no flavor or fragrance compound is lost to the environment. Still another advantage is the economy in manufacturing the flavor or fragrance compounds of the invention, since the same technology is used for all flavors and fragrances.

The objectives and other advantages of this invention will be further understood with reference to the following detailed description and examples.

## 10 DETAILED DESCRIPTION

In a preferred practice of the invention, microcapsules containing a desired flavor or fragrance compound are formed by a coacervation process. In coacervation, there is separation of a colloid into a colloid-rich phase (the coacervate) and an aqueous solution of the coacervating agent (the equilibrium liquid), forming an oil coated with protein, carbohydrate, or polymeric droplets so as to suspend the oil in water. In the process, two lipid phases and one aqueous phase are ultimately absorbed into one lipid phase and one aqueous phase. The first lipid phase forms the microcapsule core. The core is surrounded by a hydrogel capsule, defined herein as a colloid in which the dispersed phase (colloid) has combined with the continuous phase (water) to produce a viscous jellylike product. The core consists of an oil which is a term used herein to define a wide range of substances

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that are quite different in their chemical nature. Oils may be classified by their type and function and encompass mineral oils (petroleum or petroleum-derived), vegetable oils (chiefly from seeds and nuts), animal oils (usually occurring as fats; the liquid types include fish oils),

5 essential oils (complex volatile liquids derived from flowers, stems, leaves, and often the entire plant), and edible oils (chiefly vegetable oils as well as some special fish oils). Oils derived from living organisms are chemically identical with fats, the only difference being one of consistency at room temperature. In one embodiment, the oil may be

10 mineral oil, vegetable oil, or benzyl alcohol. In a preferred embodiment, the oil is a short chain triglyceride of fractionated coconut oil, available under the tradenames MigyloI® (Huls Corp., Piscataway, NJ) or Captex® (Abitec Corp., Janesville, WI). The hydrogel shell may be either carbohydrate, protein, or a synthetic polymer such as polyvinyl

15 pyrrolidone or methyl cellulose. In a preferred embodiment, the oil is MigyloI® or Captex® and the shell is gelatin. The second lipid phase is the desired flavor or fragrance compound, which is to some extent both water-soluble and lipid-soluble, that is, it is amphiphilic, which is the term used herein to define its dual solubility properties. The aqueous

20 phase is used to transport, by partition coefficient equilibrium, the slightly water soluble flavor or fragrance compound into the oil core of the microcapsule by aqueous diffusion. Equilibrium dynamics continue

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until the three phases (two lipid and one aqueous) are absorbed into two phases (one lipid and one aqueous).

For some water soluble compounds, less water is required for absorption or partitioning into the oil phase. Conversely, for some highly lipid soluble compounds, more water may be required for partitioning into the oil phase. Thus, by transiently varying the amount of water that is available to a compound, taking into account the compound's partition coefficient, a compound may be absorbed through the hydrogel shell into an oil.

Adsorption of the compound in the oil can be controlled. Dehydration of the microcapsule or crosslinking of the capsule shell locks the flavor or fragrance compound inside the microcapsule. In dehydration, a substantial volume of the water is removed from the capsule, thereby reducing the loss of the partially water-soluble flavor or fragrance compound from the oil core into an aqueous environment. Alternatively, crosslinking of the hydrogel shell of the coacervate renders the encapsulated oil thermostable, since a capsule containing crosslinks is a stable structure. The use of known chemical crosslinking agents, such as formaldehyde or glutaraldehyde, to irreversibly crosslink the oil-containing capsule is known. Other crosslinking agents such as tannic acid (tannin) or potassium aluminum sulfate (alum) are similarly known. An optional capsule hardening step, as disclosed in U.S. Patents no. 2,800,457 and 2,800,458, consists of

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adjusting a suspension of capsular material to pH 9 to 11, cooling to 0°C to 5°C, and adding formaldehyde. Formaldehyde and glutaraldehyde are also effective chemical crosslinking agents. For the food industry and the cosmetic/toiletry industries, suitable cross-linking agents may be selected depending upon the specific application.

Certain naturally-occurring enzymes are also good cross-linking agents. Crosslinking using enzymes, such as transglutaminase, is disclosed in co-pending application Serial No. 08/791,953 entitled Enzymatically Protein-Encapsulating Oil Particles by Complex Coacervation, which is hereby incorporated by reference in its entirety. Enzymes work by catalyzing the formation of bonds between certain amino acid side chains in proteins. In addition, because the enzymes are naturally occurring, encapsulated oils that are enzymatically crosslinked do not suffer from the problems inherent with formaldehyde and glutaraldehyde crosslinking, and hence may be ingested or applied without the concern of toxicity of the crosslinking agent. Because crosslinking is a enzyme catalyzed reaction, however, the proper environmental conditions must exist for optimum enzyme activity.

For compounds with high water solubility, defined herein as at least about 20% water soluble, it is preferable to concentrate the microcapsule to 55% solids or to start with dry microcapsules and gravimetrically add water and compound to get the desired results. For

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compounds with low water solubility, defined herein as less than about 20% water soluble, a hydrated microcapsule preparation may be used.

#### EXAMPLE 1

Blank capsules that are hydrated are prepared by pre-  
5 warming deionized water to  $50^{\circ}\text{C} \pm 2^{\circ}\text{C}$ . A gum solution is prepared by vigorously agitating prewarmed deionized water (87.2018 g), carboxymethyl cellulose, sodium salt (1.8447 g), and gum arabic FCC powder SP Dri (0.1845 g). The solution is mixed until the solids are completely dissolved, then the solution is cooled to about  $35^{\circ}\text{C}$  to  
10 about  $40^{\circ}\text{C}$ . A gelatin solution is prepared by vigorously agitating prewarmed deionized water (163.0453 g) and 250 Bloom type A gelatin (18.4461 g) in a preemulsion tank until the gelatin is completely dissolved, then the solution is cooled to about  $35^{\circ}\text{C}$  to about  $40^{\circ}\text{C}$ . Without agitation, the gum solution is added to the gelatin solution in  
15 the preemulsion tank and the foam is allowed to dissipate for about 15-20 min. The pH is adjusted to about 5.5 with either a dilute sodium hydroxide solution (50% w/w) or a dilute citric acid solution (50% w/w).

Vegetable oil (180.02 g of Captex® 355 mixed  
20 triglycerides or Miglyol®) is added with slow agitation, avoiding pooling of the oil. The capsule size is adjusted to about 100 microns to about



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400 microns and the size is verified microscopically. The solution is slowly cooled at about 1°C per 5 min until the solution reaches about 28°C. If the capsule walls are intact, as determined by microscopic examination of capsules showing uniform deposition of protein with no free protein floating in the water phase, the solution may be quickly cooled to about 10°C. If the capsule walls are thin, as determined by microscopic examination of capsules showing nonuniform deposition of protein and free protein floating in the water phase, the solution is reheated to about 32°C to about 33°C. The solution is mixed at about 5°C to about 10°C for 1 h. The solution is then heated to about 15°C to about 20°C. Fifty percent glutaraldehyde is added and allowed to mix for about 16 h. Agitation is then discontinued and the capsules are allowed to separate by flotation. Approximately 48% to 50% (approximately 379 lbs to 395 lbs) of water is drained from the bottom of the tank into a separate vessel. If capsules are present in the drained liquid, draining is stopped and agitation is begun to resuspend the separated capsules into solution. The separation step is then repeated. Once separation is complete, agitation is again begun in order to resuspend the capsules into solution. Sodium benzoate (10% w/w) is added with thorough mixing. If necessary, citric acid is added to adjust the pH to less than 4.0.

Blank capsules, defined herein as encapsulated oil with no flavor or fragrance value, that are dry are prepared by the following

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method. A syloid solution is prepared by mixing a silica compound syloid 244 grade 68 powder (15.9497 g) with deionized water (143.5477 g) until the powder is completely dispersed and no lumps are present. The flavor is mechanically mixed until smooth, then the  
5 syloid solution is mixed with the flavor until it is completely dispersed with no lumps, thinning out after about 30 min of stirring. The product is concentrated by centrifugation to about 50% or more solids. The material is then dried in either a vacuum oven dryer at about 80°C or in a fluid bed dryer at about 70°C.

10 The dry crosslinked capsules (400 g) are placed in a stainless steel mixing bowl (Hobart Lab Scale Mixer). The desired neat flavor (428.6 g) is mixed with deionized water (171.4 g) on a magnetic stirrer for 5 min. The dry capsules are mixed with the water/flavor mixture on the Hobart Mixer at power level 1-2 for 5 min. The mixture  
15 is poured into a plastic storage container, using a rubber spatula to scrap the sides of the mixing bowl, and the container is closed. The mixture is allowed to incubate for 24 h for flavor absorption before the product is used.

## EXAMPLE 2

20 Blank capsules that are hydrated are prepared by pre-warming deionized water to 50°C  $\pm$  2°C. A gum solution is prepared by vigorously agitating prewarmed deionized water (87.2018 g), carboxymethyl cellulose, sodium salt (1.8447 g), and gum arabic FCC

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powder SP Dri (0.1845 g). The solution is mixed until the solids are completely dissolved, then the solution is cooled to about 35°C to about 40°C. A gelatin solution is prepared by vigorously agitating prewarmed deionized water (163.0453 g) and 250 Bloom type A gelatin (18.4461 g) in a preemulsion tank until the gelatin is completely dissolved, then the solution is cooled to about 35°C to about 40°C. Without agitation, the gum solution is added to the gelatin solution in the preemulsion tank and the foam is allowed to dissipate for about 15-20 min. The pH is adjusted to about 5.5 with either a dilute sodium hydroxide solution (50% w/w) or a dilute citric acid solution (50% w/w).

Vegetable oil (180.02 g of Captex® 355 mixed triglycerides or Migylol®) is added with slow agitation, avoiding pooling of the oil. The capsule size is adjusted to about 100 microns to about 400 microns and the size is verified microscopically. The solution is slowly cooled at about 1°C per 5 min until the solution reaches about 28°C. If the capsule walls are intact, as determined by microscopic examination of capsules showing uniform deposition of protein with no free protein floating in the water phase, the solution may be quickly cooled to about 10°C. If the capsule walls are thin, as determined by microscopic examination of the capsules showing nonuniform protein deposition and free protein in the water phase, the solution is reheated to about 32°C to about 33°C. The solution is mixed at about 5°C to

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about 10°C for 16 h, then agitation is discontinued and the capsules are allowed to separate by flotation. Approximately 48% to 50% (approximately 379 lbs to 395 lbs) of water is drained from the bottom of the tank into a separate vessel. If capsules are present in the  
5 drained liquid, draining is stopped and agitation is begun to resuspend the separated capsules into solution. The separation step is then repeated. Once separation is complete, agitation is again begun in order to resuspend the capsules into solution. Sodium benzoate (10% w/w) is added with thorough mixing. If necessary, citric acid is added  
10 to adjust the pH to less than 4.0. The capsules are stored at about 5°C to about 10°C.

The hydrated uncrosslinked beads (815.20 g) are added to a glass reactor at about 5°C to about 10°C. Stirring at about 95-100 rpm is begun while maintaining the temperature at about 5°C to  
15 about 10°C. Neat flavor or fragrance (181.8 g) is added to the glass reactor. The mixture is stirred for about 2 h at about 5°C to about 10°C to allow the flavor or fragrance to absorb into the capsules. Fifty percent glutaraldehyde (3.0 g) is then added and allowed to mix at about 15°C to about 20°C for 16 h. Sodium benzoate (10.25 g of a  
20 10% solution) is added to the reactor. Citric acid (20%) is added to adjust the pH of the solution to 3.9. The capsules are stabilized by adding a well-mixed xanthan gum/propylene glycol mixture (1 part xanthan to 2 parts propylene glycol). The mixture is stirred for about

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30 min until the capsules are stabilized. Once the capsules are stabilized, they are ready for use.

### EXAMPLE 3

Sodium alginate (8.22 g, type FD 155, Grinsted Corp.)

5 was dissolved in deionized water (300 g). The solution was stirred until homogeneous. Microcapsules (3.75 g) were added with stirring until a homogeneous phase formed. Miglyol® (99.9 g) was then added with vigorous stirring to form an oil-in-water emulsion. The emulsion was fed through a vibrating needle (1.22 mm internal diameter) that  
10 was positioned about one inch above the lowest point of an eddy generated in a glass beaker by vigorous stirring of a 4% w/w aqueous  $\text{CaCl}_2$  solution (150 ml). The flow rate of the emulsion through the needle was adjusted to prevent formation of a jet. Emulsion droplets, upon entering the  $\text{CaCl}_2$  solution, immediately gelled, yielding particles  
15 of about 800  $\mu\text{m}$  diameter. After the emulsion was added, the slurry of beads was permitted to stand for about 30 min to allow migration of calcium ions into the microcapsules. The microcapsules were dewatered at room temperature either by centrifugation or by vacuum filtration, and were subsequently dried by techniques known in the art  
20 such as vacuum oven drying or fluid bed drying.

The resulting microcapsules had a slight tendency to stick together due to the presence of some surface oil. A free-flowing, dry alginate-encapsulated flavor or fragrance compound was obtained by

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mixing the microcapsules (about 58%) and water (about 7%) with the desired flavor or fragrance compound (about 35%). The optimal absorption time is between about one hour and ten hours, depending upon the partition coefficient of the particular flavor or fragrance  
5 compound.

It should be understood that the embodiments of the present invention shown and described in the specification are only preferred embodiments of the inventors who are skilled in the art and are not limiting in any way. Therefore, various changes, modifications  
10 or alterations to these embodiments may be made or resorted to without departing from the spirit of the invention and the scope of the following claims.

What is claimed is:

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1. A method of making an encapsulated flavor or fragrance compound comprising:
  - preparing a microcapsule having a hydrogel shell surrounding an oil core,
  - 5 adding an amphiphilic flavor or fragrance compound in the presence of water to the microcapsule for transportation of the compound into the oil core,
  - transporting the compound by aqueous diffusion through the hydrogel shell into the oil core, and
  - 10 retaining the oil core in the hydrogel shell during said transportation to provide the encapsulated flavor or fragrance in the hydrogel shell containing the retained oil core.

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2. The method of claim 1 wherein the microcapsule is dried before adding the flavor or fragrance compound in the presence of water.
3. The method of claim 1 wherein the shell is selected from the group consisting of a protein, a carbohydrate, and a synthetic polymer.
4. The method of claim 3 wherein the synthetic polymer is polyvinyl pyrrolidone.
5. The method of claim 1 wherein the oil core is selected from the group consisting of a mineral oil, a vegetable oil, a benzyl alcohol, and mixtures thereof.
6. The method of claim 5 wherein the vegetable oil is a short chain triglyceride of fractionated coconut oil.
7. The method of claim 1 further comprising treating the shell to prevent removal of the flavor or fragrance compound from the microcapsule.



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8. The method of claim 7 wherein the treating is by removing water from the shell.
9. The method of claim 8 wherein the removing water is by adding a salt.
10. The method of claim 7 wherein the treating is by crosslinking the shell.
11. The method of claim 10 wherein the crosslinking is by adding a crosslinking agent.
12. The method of claim 10 wherein the crosslinking is performed before the flavor or fragrance compound is added to the microcapsule.
13. The method of claim 10 wherein the crosslinking is performed after the flavor or fragrance compound is added to the microcapsule.
14. The method of claim 1 wherein the microcapsule is prepared by coacervation of an oil core and a hydrogel shell.

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15. The method of claim 1 wherein a mixture of flavor or fragrance compounds is added to the microcapsule.
16. A product of the method of claim 1.
17. A product of the method of claim 3.
18. A product of the method of claim 5.
19. A product of the method of claim 6.
20. A product of the method of claim 14.

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21. A method of making an encapsulated flavor or fragrance compound comprising:

preparing a substantially dry microcapsule having a hydrogel shell surrounding an oil core,

5 adding an amphiphilic flavor or fragrance compound in the presence of a controlled volume of water to the microcapsule for transportation of the compound into the oil core,

transporting the compound by aqueous diffusion through the hydrogel shell into the oil core,

10 retaining the oil core in the hydrogel shell during the transportation to provide the encapsulated flavor or fragrance in the hydrogel shell containing the retained oil core, and

drying the microcapsule having the flavor or fragrance compound retained in the oil core.

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22. The method of claim 21 wherein the shell is selected from the group consisting of a protein, a carbohydrate, and a synthetic polymer.

23. The method of claim 22 wherein the synthetic polymer is polyvinyl pyrrolidone.

24. The method of claim 21 wherein the oil core is selected from the group consisting of a mineral oil, a vegetable oil, a benzyl alcohol, and mixtures thereof.

25. The method of claim 24 wherein the vegetable oil is a short chain triglyceride of fractionated coconut oil.

26. The method of claim 21 further comprising treating the shell to prevent removal of the flavor or fragrance compound from the microcapsule.

27. The method of claim 26 wherein the treating is by crosslinking the shell.

28. The method of claim 27 wherein the crosslinking is by adding a crosslinking agent.

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29. The method of claim 27 wherein the crosslinking is performed before the flavor or fragrance compound is added to the microcapsule.

30. The method of claim 27 wherein the crosslinking is performed after the flavor or fragrance compound is added to the microcapsule.

31. The method of claim 21 wherein the microcapsule is prepared by coacervation of an oil core and a hydrogel shell.

32. The method of claim 21 wherein a mixture of flavor or fragrance compounds is added to the microcapsule.

33. A product of the method of claim 21.

34. A product of the method of claim 22.

35. A product of the method of claim 24.

36. A product of the method of claim 25.

37. A product of the method of claim 31.

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38. A method of making an encapsulated flavor or fragrance compound comprising:

preparing a microcapsule by coacervation of an oil core in a hydrogel shell,

5 adding an amphiphilic flavor or fragrance compound in the presence of water to the microcapsule for transportation of the compound into the oil core,

transporting the compound by aqueous diffusion through the hydrogel shell into the core, and

10 retaining the oil core in the hydrogel shell during said transportation to provide the encapsulated flavor or fragrance in the hydrogel shell containing the retained oil core.

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 B01J13/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 096, no. 002, 29 February 1996 & JP 07 275688 A (KYOWA YAKUHHIN KOGYO), 24 October 1995 see abstract	
A	<p>---</p> <p>DATABASE WPI Section Ch, Week 950225 October 1994 Derwent Publications Ltd., London, GB; Class A, Page 14, AN 95-010988 XP002086111 &amp; JP 06 296856 A (KYOWA YAKUHHIN KOGYO) , 25 October 1994 see abstract</p> <p>---</p> <p style="text-align: center;">-/--</p>	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication where appropriate, of the relevant passages	Relevant to claim No.
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International Application No

PCT/IB 98/01551

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